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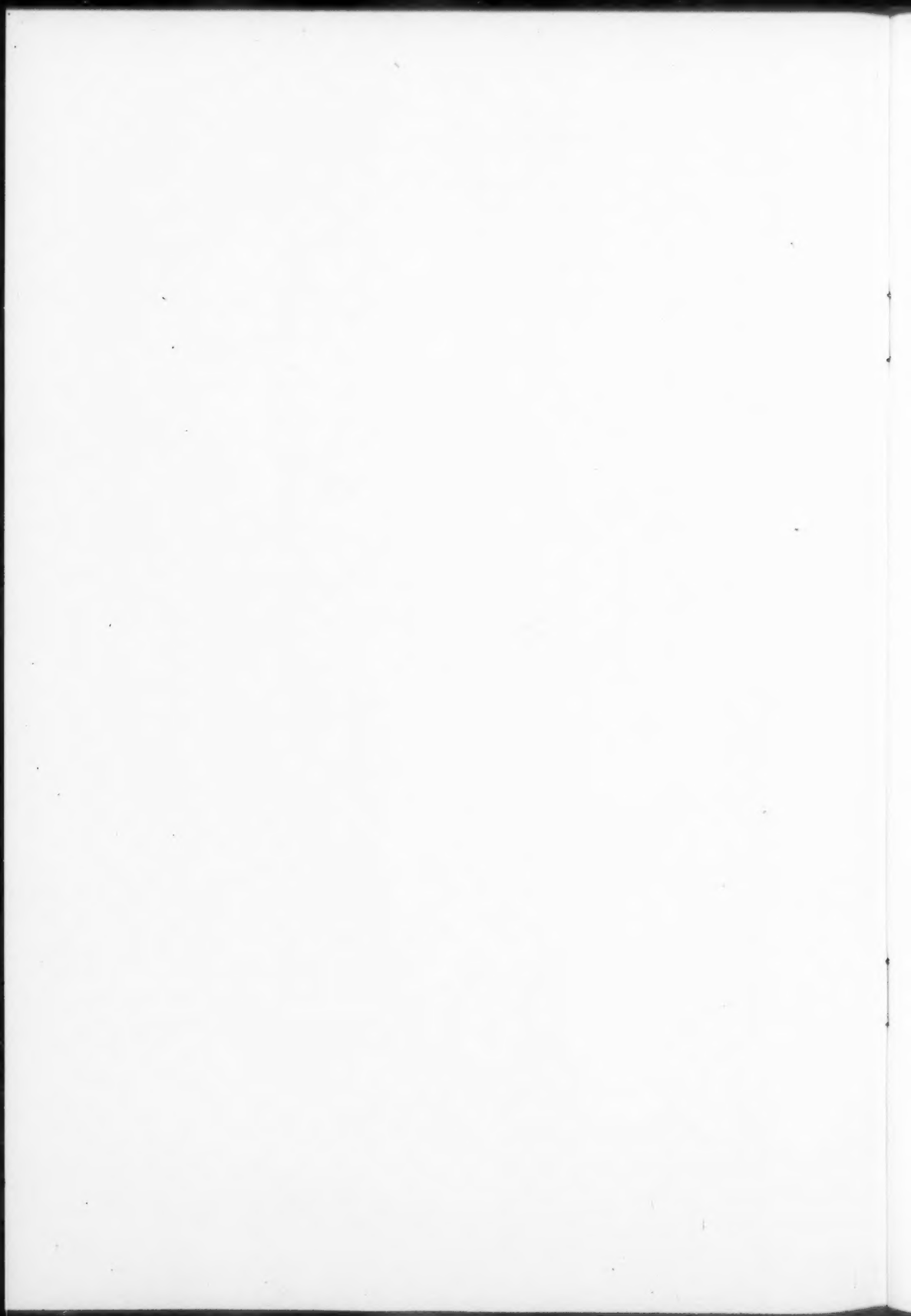
EDITOR'S NOTE

Material scheduled for publication in this issue will appear later.
This title page is included for purposes of record.

THE EFFECT OF GEL WATER ON CATALYTIC ACTIVITY

III. THE DECOMPOSITION OF FORMIC ACID OVER ALUMINA[1]

BY L. A. MUNRO[2], D. J. DEWAR[3], S. GERTSMAN[4],
AND G. MONTEITH[5]

Abstract

The effect of gel water content on the catalytic activity of alumina in the decomposition of formic acid at 215 and 250° C. has been investigated. The previous observations on the dehydration of ethyl alcohol to ether and ethylene are paralleled by the results with formic acid. There are two peaks in the curves showing the relation between activity and gel water content. The ratio CO/CO_2 changes with gel water content, i.e., the course of the reaction can be altered by surface modification of the catalyst. The gel showing maximum catalytic activity exhibits greatest sorption. The temperature of activation of a hydrous oxide is not as accurate a measure of the catalytic power as the gel water content. X-ray studies of the catalysts show a threefold change in the structure in the 36 to 0% range of water content, but the fibril structure of the gel of maximum activity (5.3% water) is the same as that for minimum activity. An explanation is suggested.

Some years ago it was found that the extent of the sorption of gases and vapours by an alumina gel varied with the amount of residual gel water (15, 16, 17). Maximum sorption occurred at a specific gel water content differing for each sorbate. Similar observations have been made by Lamb and Woodhouse (13) on the sorption of gases by a natural zeolite, the optimum sorptions of hydrogen, oxygen, and carbon dioxide occurring at 1.2, 3.1, and 7.1% gel water, respectively.

It was thought therefore that the activity of a hydrous oxide catalyst at a fixed temperature would probably be a maximum at some definite water content. This expectation was realized in the catalytic preparation of ether and ethylene from ethyl alcohol (2, 14) and in the reaction of carbon disulphide and water to give, by a chain of reactions, hydrogen sulphide and carbon dioxide (17).

In the experiments with alcohol, it was found that an alumina catalyst at 250° C. caused the production of ether only. With the gel containing 5.3% water there was a sharp maximum. In later experiments at 318°, in which

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both ethylene and ether were produced, the total decomposition showed two maxima—at 1.3 and 5.3% gel water, corresponding to the most active catalysts for the production of ethylene and ether, respectively. The ratio of ethylene to ether increased to a maximum at approximately 2%, decreasing considerably for catalysts of zero water content.

In the reaction between carbon disulphide and water, the sample of catalyst giving maximum sorption of carbon disulphide was not the one of maximum activity. The results were interpreted to mean that the removal of water from the catalyst gave, at a certain point, an optimum arrangement of adsorbed carbon disulphide and water molecules on the surface. Too much adsorption of either reactant or an unfavourable arrangement of the activated spots or points on the catalyst decreased the catalytic activity.

If two or more reactions are possible, the changes in the surface concomitant with loss of gel water might favour first one and then another of the reactions. The decomposition of formic acid was chosen as a means of testing this. It can decompose in four ways:

1. $HCOOH \longrightarrow CO_2 + H_2$
2. $HCOOH \longrightarrow CO + H_2O$
3. $2\,HCOOH \longrightarrow HCHO + CO_2 + H_2O$
4. $3\,HCOOH \longrightarrow CH_3OH + 2CO_2 + H_2O.$

The temperature of the catalyzed reactions is sufficiently low to allow the use of catalysts having a wide range of gel water content. The study was also undertaken to see whether the catalysts gave, for the chief reaction (dehydration), an optimum point similar to that found in the above experiments.

Decomposition of Formic Acid

The literature contains a considerable number of papers on the decomposition of formic acid in the liquid and vapour phases using various catalysts. Of these, several pertinent to the present problem may be cited briefly.

The first comprehensive study was made by Sabatier and Mailhe (19). According to these workers, the decomposition over alumina began at $234°$ C. and yielded mostly carbon monoxide, with 6% of carbon dioxide and some formaldehyde; i.e., alumina was essentially a dehydration catalyst. Catalysts of mixed function included glass, pumice, lime, iron oxide, and thoria. Methyl alcohol was obtained in appreciable quantities above $340°$, using thoria.

Adkins (1) passed formic acid at a relatively high rate over different alumina catalysts. He concluded that catalysts having large pores favoured decarboxylation, while those having small pores favoured dehydration.

Nelson and Engelder (18) showed that the catalyst tube or container might itself catalyze one or other of the decomposition reactions. Formic acid passed through tubes of glass, Pyrex, porcelain, and copper gave chiefly carbon dioxide and hydrogen. Pyrex was the least active.

Clark and Topley (4) report a very slight decomposition over Pyrex at $200°$ C. yielding chiefly carbon monoxide.

Westcott and Engelder (24) passed formic acid at 10 cc. per hr. over alumina in unglazed clay tubes. At 280° and 310° C. the products contained 92% of carbon monoxide, 5% of carbon dioxide, and 3% of hydrogen. At 373°, approximately equal volumes of the three gases were obtained.

Tropsch (21) found, in contrast with the results of Westcott and Engelder, that in the range of temperature from 305° to 435° the alumina caused the production of carbon monoxide and water exclusively. He also reported that this was independent of the dryness of the acid.

Graeber and Cryder (7) found that the efficiency of the decomposition over alumina and other catalysts increased with increasing space velocity until a limiting value was obtained. They considered any carbon dioxide and hydrogen to be due to secondary reactions.

It will be seen from the above brief review that there is considerable disagreement in the data on the catalytic decomposition of formic acid over alumina. Adkins' conclusions have been questioned by Bancroft and George (3). Moreover, in some cases small amounts of the catalyst were supported on pumice, which at the temperatures used would itself catalyze the decomposition to carbon dioxide and hydrogen. At the higher temperatures used by Westcott and Engelder (24), the glass tube acted in the same way. Furthermore, the alumina used was activated at 250° C. and then used at higher temperatures, so that further activation with the liberation of water and changes in the surface and in the crystal structure would occur. In all the above work, the effect of gel water has not been considered.

It is clear that to obtain comparable results the rate of input and the temperature of the catalyst must be constant. The effect of the tube or support must be relatively small and constant, and changes in the catalyst during the reaction should be kept at a minimum. In the present study of the efficiency of catalysts differing in gel water content, all these factors have been controlled.

Material

The best analytical grade of formic acid was used. In the experiments of Series 1 and 2, the acid used was 98 to 100% pure. In Series 2, 90% (aqueous) formic acid was used in comparative runs. All samples gave negative tests for aldehyde.

Preparation of the Catalysts

In the first series of experiments, the catalyst was prepared from the best grade of aluminium nitrate. In the second series, the chloride was used, and the method of Willstätter (25) for his " 'C' hydroxide" was followed. The dried gel was broken up to 19 to 28 mesh. Equal amounts of a well mixed sample were used to fill each catalyst tube. These tubes were of Pyrex and of the same size to give a constant space velocity.

Catalysts differing in gel water content were obtained by heating the tubes of gel at selected temperatures from 250° to 450° C. for one hour in a stream of nitrogen. The amount of water lost was found by weighing the tubes before

and after activation. The total or initial water content of the batch was determined by blasting weighed samples over a Méker burner for 36 to 48 hr. to constant weight. Equivalent amounts were withdrawn from each sample of catalyst for X-ray study of fibril lattice.

Apparatus

The apparatus used is shown in Fig. 1. It consists of an arrangement for the addition of the formic acid to the catalyst at a constant rate, a vaporizer, a controlled furnace, and receivers for liquid and gaseous products.
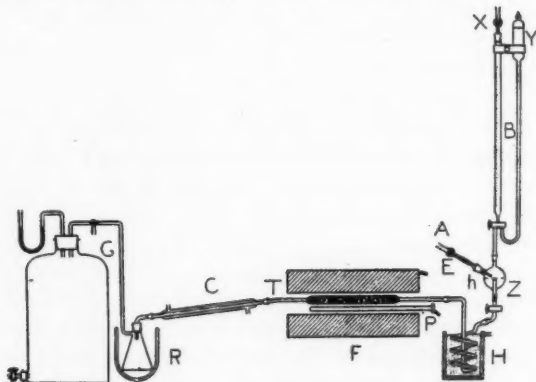
FIG. 1. *Apparatus.*

In operation, the acid from a sealed 100 cc. ampoule is introduced into bulb Y, which is used to fill the burette, B. This is connected by a three-way stopcock to a constant flow apparatus, Z, essentially that described by Corson (5). The 50 cc. bulb is provided with an overflow tube at its centre and a capillary side tube, A, with a calcium chloride tube, E, to admit dry air. A fine capillary or later a packed plug of Pyrex glass wool or asbestos of the required thickness is inserted between the stopcock and the bulb. The bulb and the overflow tube are filled from the stopcock to the level h. This can be done accurately by emptying it until a meniscus appears in the exit tube at that level.

A 10 cc. sample is then introduced from the burette, the stopcock opened at zero time, and closed when the meniscus again appeared at level h. Preliminary experiments showed that this apparatus delivered a constant volume of liquid for each run, and that the duration of the run was constant to within 2%. The rate of flow was uniform during delivery.

The formic acid passing through the stopcock enters a preheater kept at a temperature of between 210° and 215° C. The vaporized acid then enters the catalyst tube, which is maintained at the chosen temperature, within one degree as determined by a pyrometer. Any undecomposed formic acid and liquid products are condensed and collected in a receiver in a Dewar flask.

The gaseous products are collected in a gasometer at atmospheric pressure by controlling the outflow of saturated brine from the bottom of the gasometer.

Since carbon dioxide is moderately soluble in saturated brine solution the procedure of W. A. Lutz* was employed. Small amounts of sodium carbonate were added to the brine and the solution was made slightly acid with sulphuric or hydrochloric acid, thus causing the evolution of the carbon dioxide. The solution was allowed to stand overnight open to the air and was stirred vigorously before use to remove any excess gas. Lutz stated that such a procedure caused negligible losses of carbon dioxide from samples containing up to 5% of the gas, and less than 1% from those containing 20%.

Analysis of the Products

Gas analysis for carbon dioxide, oxygen, hydrogen, and carbon monoxide was carried out with the Fischer Universal gas analyser. Undecomposed formic acid was determined by titrating an aliquot of the condensate. Traces of formaldehyde were detected in the low temperature runs, and amounts were estimated by adding 1 cc. of Schiff's reagent to a standard quantity of condensate and comparing the colour with that of standard solutions.

Experimental Results

A few runs were made at 360° C. Decomposition at this temperature was 100%. No formaldehyde was obtained. Analysis of the gaseous products varied between the following limits: CO, 87 to 91; CO_2, 4.5 to 6.5; H_2, 4.5 to 6.5%. These are essentially the same as those reported by Westcott and Engelder (24) at 310°. Gas samples removed during the course of the reaction had the same composition as those taken from the gasometer at the completion of the run; this indicated that the carbon dioxide loss was not appreciable.

A blank run on the catalyst tube alone yielded carbon dioxide and hydrogen in amounts equal to the total amount found in the runs with the alumina present. This confirms the findings of Tropsch that at this temperature the action of alumina is wholly one of dehydration.

In a blank run at 215° C. the total decomposition was only 0.7%, the gas produced being largely carbon monoxide. This temperature was accordingly chosen for Series 1.

With a series of gels whose water content ranged from 18% to 0%, it was found that, in contrast to the results obtained with the alumina used by Sabatier and Mailhe (19), there was appreciable decomposition of the formic acid. The amount of carbon monoxide varied with the gel water content from 6.4 to 26.8%; carbon dioxide, from 0.25 to 0.80%; hydrogen, from 0.04 to 9.23%; and formaldehyde, from 0.05 to 0.15%.

* *See page 829 of Reference (7).*

The results for the first and second runs with the same catalysts are given in Fig. 2. The curves show the change in the percentage of the acid decomposed to carbon monoxide with catalysts of different gel water content. The values for carbon dioxide (0.28 to 0.91 mole per cent) and for hydrogen (0.04 to 0.27 mole per cent) were so small that they have been omitted. The values of the CO/CO_2 ratio, which may indicate any change in the reaction, are shown in Fig. 4. Both A and B runs showed a sharp increase in the ratio for the catalyst containing no water, although the activity of this catalyst for both the carbon monoxide and carbon dioxide production was low. The ratio also increases for the catalyst showing a maximum activity. The effect for the remaining portion of the curve is undoubtedly masked owing to the large over-all production of carbon monoxide.
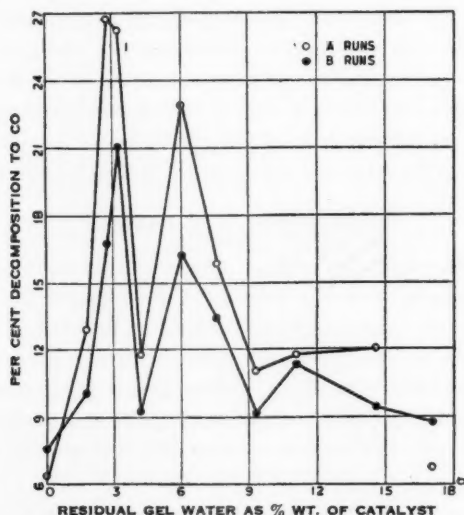
FIG. 2. *Percentage decomposition to carbon monoxide. Comparison of A and B runs, Series 1.*

In the second series of experiments, the reaction temperature was raised to 250° C. The alumina gel was prepared from the chloride, and 90% (aqueous) formic acid was used. The results are shown graphically in Fig. 3, Curve 2. It will be seen that this curve is essentially similar to those previously obtained. In Fig. 5, the curve for total decomposition of formic acid is compared with a similar curve for ethyl alcohol. Both show a decided maximum at about 5% gel water. With this series of runs, however, the ratio of dehydration to decarboxylation reactions, as shown by the CO/CO_2 values (Fig. 6), was much higher than in Series 1 and 3. The dehydration reaction increased continuously until the value for the catalyst of 2.7% moisture content was reached; it then fell sharply to the value for the catalyst
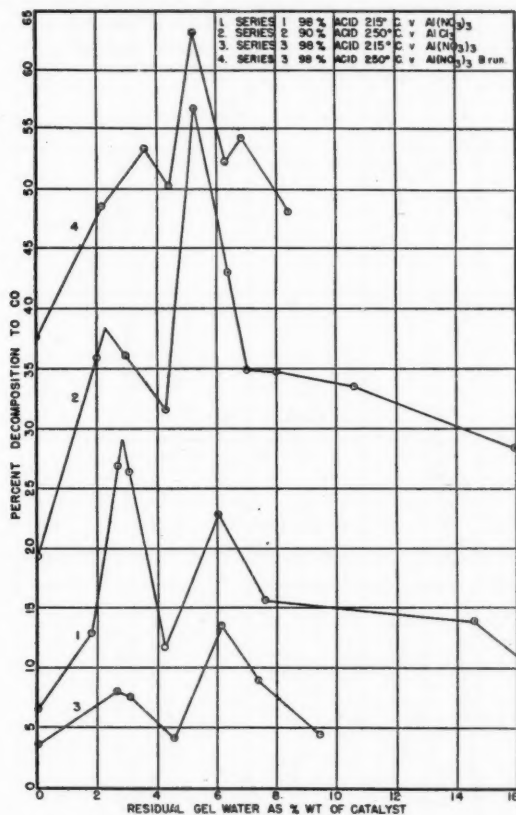
FIG. 3.   *Comparison of A runs for different series of catalysts.*

of zero water content.   This is in contrast with the periodic shift in reaction as shown in Series 1, Curves 1A and 1B, Fig. 4, and for the ethylene–ether ratio of previous studies.

Series 3 was undertaken to establish more exactly the position of peak activity for this reaction.   The results of these experiments are shown in Curves 3 and 4 of Fig. 3 and Curves 3A and 3B in Fig. 4.   These indicate substantially the same catalyst behaviour as was found in Series 1.   Here again the CO/CO_2 ratio increases at the first peak (about 3%) and at zero water content.

Desorption

In most cases a drop in activity is noted in the second runs.   This drop is usually most pronounced with those catalysts showing peak activity, a fact attributed to deactivation of a portion of the surface by adsorption of water or formic acid, or both.   In Series 2, adsorption was measured by determining
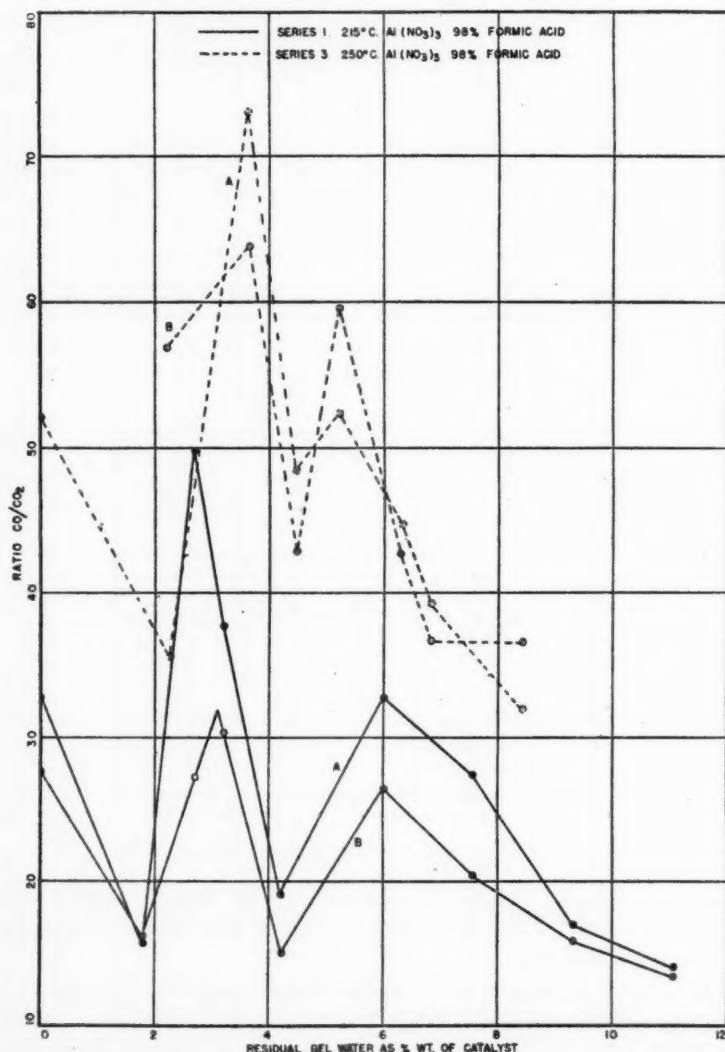
FIG. 4. *The ratio of dehydration to decarboxylation for Series 1 and 3.   Full lines, Curves 1A and 1B.   Broken lines, Curves 3A and 3B.*

the increase in weight of the catalyst after two runs.   Desorption was carried out by passing dry nitrogen through the tube for 1.5 hr. at 250° C.   Preliminary experiments showed that these conditions gave constant weight in all cases.   The desorption procedure caused further activation only in the case of catalysts that contained more than 11% of water.   Such gels are probably altered during the catalytic reaction at the higher temperature.
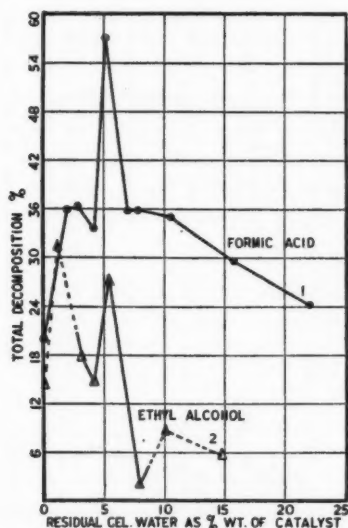
FIG. 5.   Comparison of the effect of gel water on catalytic activity with two different react-ants.
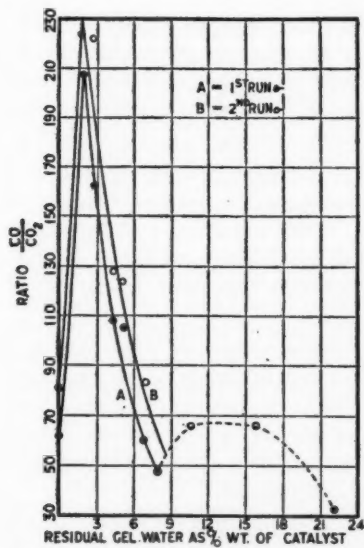
FIG. 6.   Series 2.   Ratio of dehydration to decarboxylation.

In Fig. 7, Curve 1 shows the amount in grams desorbed per gram of catalyst. Curve 2 gives the amount of adsorption.   It coincides with Curve 1 for gels containing from 5 to 10% of water.   It will be seen that in this series the most active catalyst is also the most active sorbent.
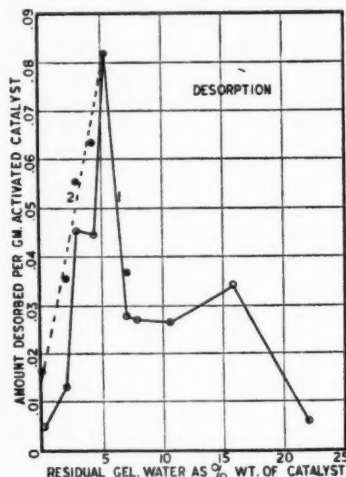
FIG. 7.   *Curve 1, amount desorbed.   Curve 2, amount sorbed (grams per gram of catalyst).*

Discussion

These results, obtained by different experimenters over a period of years using different samples of alumina, show that the adsorptive and catalytic activity of a hydrous oxide are indicated or determined to an important degree by the amount of gel water.   Further, if two reactions are possible the same associated factors will influence the course or direction of the reaction.

Since the beginning of this work, it was discovered that Hüttig and Garside (11) had made similar observations on the chemical and catalytic activity of ferric oxide hydrogel.   They obtained a sharp optimum activity at about 12% of water (1.2 moles).   Ewing and Bauer (6) have found that the heat of wetting of silica gel was a maximum when the gel contained 4% of gel water.

In the decomposition of formic acid into carbon dioxide and hydrogen, Hinshelwood and Topley (10) found no relation between the activation energy and the velocity of the reaction, but the calculated fraction of catalyst surface available paralleled the decomposition velocity.   Hinshelwood and Hartley (9) observed that the nature of a glass catalyst influenced both the velocity and direction of the decomposition.

A periodic fluctuation was observed by Hüttig *et al.* (12) when the catalytic activity of a series of mixed oxide catalysts (zinc oxide and ferric oxide) was plotted against the temperature of activation.   Two peaks were obtained for the combustion of carbon monoxide and almost the same curves for the decomposition of nitrous oxide.

All the above work lends support to the thesis that surface factors, such as favoured arrangement of free spaces or adsorption stations indicated by

optimum contents of gel water, are of prime importance in determining catalytic activity.

The temperature of activation cannot be used with different preparations of the same catalyst to predict catalytic activity with accuracy. The great variety of "optimum" temperatures for any one catalyst in the literature is evidence of this. The amount of gel water left after activation is a much better criterion. This is illustrated in Fig. 8.
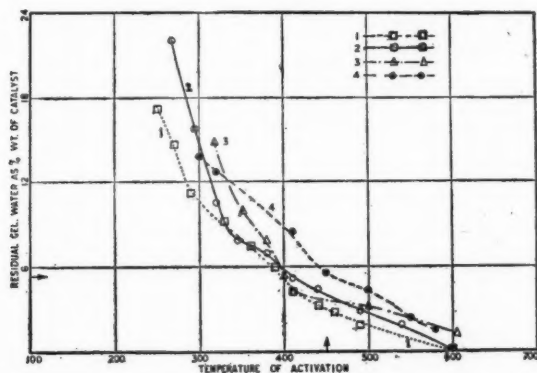
FIG. 8.   *Variation of gel water content with temperature of activation for different samples of alumina.   Curve 1, Series 1.   Curve 2, Series 2.   Curve 3, gel used by Alexander, Horn, and Munro (2).   Curve 4, gel used by Munro and Horn (14).*

The water–temperature curves are for four aluminas. Curve 1 represents the alumina used in Series 1 experiments; Curve 2, for Series 2; Curve 3 for preparations used by Alexander, Horn, and Munro (2) and Curve 4 for those used by Munro and Horn (14).

Suppose a specific temperature of activation, e.g., 450° C., indicated by an arrow in the figure, is selected. The curves show that the catalysts contained 2.8, 4.0, 4.3, and 6.0% of gel water. These catalysts differ greatly in activity. Reference to Curves 1 and 2, Fig. 3, shows that the gel containing 4.3% of water had a low activity while that containing 2.8% had a much higher activity.

Or again, consider a definite water content, e.g., 5.3%; the results of Horn and Alexander show that the temperature of activation differed by 50°. The catalytic activities of these gels however were comparable in that they both gave sharp peaks at this point in the curves for the dehydration of alcohol to ether.

Heat treatment of a gel may cause other changes besides the removal of water and increase in available or active surface. It accelerates the process known as ageing. This process of heat ageing produces changes in the crystal structure of the gel fibrils. Weiser and Milligan (23) give numerous examples of this.

In order to determine whether the pronounced periodic fluctuation in activity of the alumina corresponded to the development of a new lattice phase, X-ray photographs were taken of several powdered samples whose gel water contents were in the range studied. These samples comprised catalysts of the following water contents: 0%, 5.3% before use, 5.3% after use, 4.2%, and the original air-dried unactivated gel. The results are shown in Fig. 9.

An examination of the prints shows that three different forms are obtained. The three middle gels belong to one type; the sample that had been blasted and the unactivated samples to two other structures—the carborundum and trihydrate respectively.

This means that the peaks and depressions in the catalysis curves cannot be explained on the basis of lattice structure. This finding agrees with that of Smith and Hawk (20), who obtained no characteristic lines for their catalyst corresponding to observed increased activity in the decomposition of methyl alcohol over an oxide catalyst. Griffith and Hill (8) reported similar results, although in their studies they used promoted catalysts.

The decrease in activity of the gel as the carborundum lattice is formed may be due to a decrease in surface caused by sintering or to structural changes.

These results indicate that the maxima and minima in the activity of hydrous oxide catalysts are determined by factors related intimately to the residual gel water, such as the extent, potential, and geometry of the free surface spaces liberated during activation.

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PLATE I
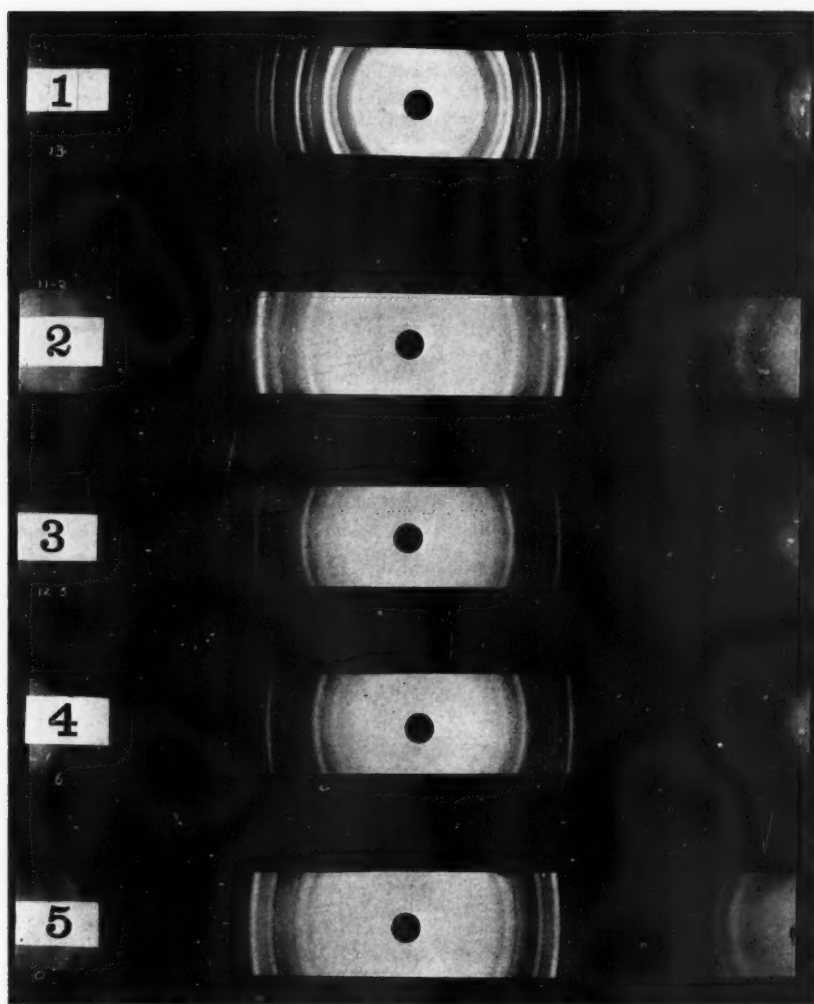
FIG. 9.   *X-ray photographs.*
   1. Catalyst containing 0% water.
   2. Catalyst containing 5.27% water before use.
   3. Same catalyst (2) after use.
   4. Catalyst containing 4% of water.
   5. Unactivated alumina gel.

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THE HYDRATION OF THE ALUMINATES OF CALCIUM

III. THE HYDRATION OF THE 5 : 3, 1 : 1, AND 3 : 5 CALCIUM ALUMINATES[1]

BY W. G. SCHNEIDER[2] AND T. THORVALDSON[3]

Abstract

The hydration of the aluminates of calcium in saturated steam at 150° and 105° C. was studied. A method was developed for the quantitative estimation of chemically combined and free hydrated alumina in steam treated mixtures. The rates of hydration at 150° C. of all the aluminates of calcium were compared. At 150° C., when conditions favouring rapid hydrolysis are avoided, the 1 : 1 and 3 : 5 lime aluminates are apparently transformed almost quantitatively to the cubic hexahydrate of tricalcium aluminate and hydrated alumina approaching the composition of the monohydrate. The steam treated 5 : 3 lime aluminate gives lower water absorption and higher content of combined alumina than called for by the above end-products, indicating the formation of a less highly hydrated aluminate of lower lime–alumina ratio than the hexahydrate of tricalcium aluminate. This conclusion is supported by the presence in this product of some anisotropic material with an average refractive index of 1.58. The hydrothermal products obtained on treatment of the three aluminates at 105° C. all contained larger amounts of this birefringent material and apparently a greater proportion of combined alumina.

Introduction

The increased use of hydrothermal methods in the manufacture of certain building materials has led to greater interest in the chemical and physical changes that compounds containing lime, alumina, and silica undergo during such processing. Several studies dealing with the hydrothermal treatment of the aluminates of calcium have been made (7). It is generally considered that tricalcium aluminate is hydrated directly to the hexahydrate, while the other aluminates give this same compound together with hydrated alumina. Except in the case of tricalcium aluminate there is, however, lack of quantitative data supporting these conclusions.

Preliminary experiments made by Norman S. Grace (3) on the gain in weight of the 5 : 3 calcium aluminate, monocalcium aluminate, 3 : 5 calcium aluminate, and precipitated alumina when exposed to saturated steam at 150° C., with subsequent drying over calcium oxide, indicated that the hexahydrate of tricalcium aluminate and a monohydrate of alumina are probably formed. The 5 : 3 aluminate was found to hydrate slowly and the absorption of water was somewhat lower than that calculated on the above basis, while the amounts absorbed by the monocalcium aluminate and the 3 : 5 calcium aluminate were slightly above the calculated values. As the aluminates used by Grace had been prepared from commercial materials in

an oil-fired furnace, it was deemed advisable to make a more careful study with aluminates of the highest purity and to attempt to determine combined and uncombined alumina in the treated materials as a further quantitative check on the end-products of the hydrothermal treatments.

Lately the correctness of the composition usually assigned to two of the anhydrous aluminates, namely, the 5 : 3 and the 3 : 5 calcium aluminates, has been questioned and the alternative formulae, $12CaO \cdot 7Al_2O_3$ and $CaO \cdot 2Al_2O_3$, respectively, suggested (1, 2, 4, 6, 8). The experiments described in this paper were made with products of the former compositions. The results and calculations would, however, apply irrespective of the actual formulae, provided all the aluminates react on hydrothermal treatment to give the same final products, or as an alternative, if the calculations were made on the assumption that the 5 : 3 composition contains 94.5% $12CaO \cdot 7Al_2O_3$ with 5.5% $CaO \cdot Al_2O_3$ and the 3 : 5 composition 76.7% $CaO \cdot 2Al_2O_3$ with 23.3% $CaO \cdot Al_2O_3$. The conclusions as to the rates of hydration might, however, be subject to some change.

Experimental

Preparation of the Aluminates

These were prepared by the usual methods. Low alkali "Analytical Reagent" calcium carbonate was further purified by removal of traces of iron and alumina and then reprecipitated as the carbonate. Alumina prepared by double precipitation from iron-free alum was mixed with the purified carbonate in the required proportions, the mixture carefully heated in platinum crucibles in a muffle furnace to drive off the carbon dioxide and most of the water of hydration, and then ignited in an induction furnace at temperatures just below the melting point of the aluminate. Several heatings were made with intermediate grinding until the product was homogeneous as shown by a microscopic examination. The samples were finally ground to pass a 200-mesh sieve. The results of chemical analysis of the final products and the calculated composition are given in Table I together with the values obtained for the refractive indices.

The Rate of Hydration of the Aluminates of Calcium at 150° C.

One gram samples of the aluminate contained in platinum crucibles were ignited to constant weight at 950° C. and placed over water in an autoclave of hammered copper heated by a gas flame. The crucibles were protected from condensing water. After heating at 150° C. ($\pm$ 5°) for a given time, the samples were removed and dried *in vacuo* over lime to constant weight. Table II gives the results of a series of hydrations in which the same sample of each aluminate was used throughout, this being repeatedly treated in the autoclave with intermediate drying and weighing. Tricalcium aluminate is included for comparison.

The most striking observation is the very slow hydration of the 5 : 3 composition (which after 504 hours' treatment had not nearly reached constancy) as compared with that of the other three aluminates. As it was possible

TABLE I

ANALYSIS OF THE ALUMINATES

Aluminate	Sample	CaO, %	Al$_2$O$_3$, %	Refractive indices ± 0.002 (sodium light)
3CaO·Al$_2$O$_3$	A	62.24	37.80	N = 1.710
	S	62.27	37.86	N = 1.710
	Calc.	62.27	37.73	
5CaO·3Al$_2$O$_3$	137*	47.81	52.04	N = 1.608
	Calc.	47.82	52.18	
CaO·Al$_2$O$_3$	237*	35.45	64.53	α = 1.643; β = 1.655; γ = 1.633
	Calc.	35.48	64.52	
3CaO·5Al$_2$O$_3$	137*	24.76	75.10	ω = 1.617; ϵ = 1.652
	Calc.	24.81	75.19	

* Preparation by Ernest C. Bailey; all analyses by William G. Schneider.

TABLE II

THE RATE OF HYDRATION OF THE ALUMINATES OF CALCIUM AT 150° C.

Time, hr.	Percentage water taken up (on basis of original weight)			
	3CaO·Al$_2$O$_3$	5CaO·3Al$_2$O$_3$	CaO·Al$_2$O$_3$	3CaO·5Al$_2$O$_3$
1	13.14	3.43	12.94	16.28
3	24.04	4.04	15.42	18.83
6	33.35	4.82	18.36	21.35
12	37.26	5.41	21.84	23.42
24	39.18	6.96	25.98	25.69
73	39.98	9.04	29.63	28.40
144	39.98	10.55	30.32	28.40
264		13.56	30.67	
384		16.65	30.98	
504		23.52	31.35	

that the frequent drying of the samples affected materially and unequally the rates of hydration, other series of experiments were made in which each sample was treated only once. It was found that single treatments gave only slightly higher values for the absorption of water by the 3 : 1, 1 : 1, and 3 : 5 products (the maximum being the same), and that although the acceleration in the case of the 5 : 3 composition was much greater, continued treatment for 16 to 21 days (500 hr.) was necessary for attainment of constant weight (absorption of about 33% of water). The 3 : 1 and 3 : 5 products reached the maximum hydration in single three-day treatments.

A similar series of hydrations was also carried out at a temperature of 105° C. The rate of hydration was lower except in the case of the 3 : 5 composition, which, after the first hour of treatment, took up water more rapidly. The rate of hydration of the different calcium aluminates decreased in the order 3 : 5, 3 : 1, 1 : 1, 5 : 3.

It should be noted that there are two factors not directly connected with the reactivity of the aluminate with water that may affect the above comparisons. As mentioned above, there is some evidence that two of the above compositions do not represent pure compounds, namely, the 5 : 3 and the 3 : 5 calcium aluminates may have the composition $12CaO \cdot 7Al_2O_3$ and $CaO \cdot 2Al_2O_3$. The second factor is that on account of the low melting point of the 5 : 3 aluminate some fusion often takes place during its preparation, while this is usually not the case with the lower-limed aluminates and must be especially guarded against in the preparation of the 3 : 1 compound.

The Composition of Autoclaved Alumina

The effect of hydrothermal treatment of alumina at temperatures between 150° ($\pm$ 5°) and 350° C. has been previously studied in this laboratory (5). Prolonged treatment within this temperature range was found to produce a cryptocrystalline product giving a well defined X-ray powder pattern. The composition varied only slightly with the temperature of the autoclave or (except for ignition at high temperatures) with the previous history of the alumina. The molar ratio of water to alumina in the product after drying over calcium oxide varied from 1.0 to 1.1, the higher temperatures giving the lower ratio.

In order to obtain a figure for the hydration of alumina for purposes of calculation, further hydrothermal treatments in the autoclave were made at 150° C. Six 1 gm. samples, three being hydrated commercial alumina of "reagent" quality containing 35.5% of water and three being alumina prepared by double precipitation from iron-free alum, which after drying contained 30.6% of water, were used. As a preliminary treatment one sample from each group was dehydrated at 800° C. until only 0.5% of water remained. The samples were treated in the autoclave at 150° C. for 20 to 22 days and then dried to constant weight over calcium oxide. The water held varied from 1.06 to 1.16 moles, the average composition being $Al_2O_3 \cdot 1.1H_2O$. The refractive index varied from 1.62 to 1.63. The details are given in Table III.

TABLE III

COMPOSITION OF ALUMINA AUTOCLAVED AT 150° C.

Sample	Initial % H_2O	Days in autoclave	Final % H_2O, anhyd. basis	Molar ratio $H_2O:Al_2O_3$	Refractive index (± 0.005)
Commercial	35.5	20	19.60	1.11	1.635
Commercial	35.5	20	20.48	1.16	1.631
Commercial	0.5*	22	19.88	1.12	
Precipitated	30.6	20	18.72	1.06	1.619
Precipitated	30.6	20	19.17	1.08	1.619
Precipitated	0.5*	22	19.07	1.08	
Average				1.10	

* Sample ignited at 800° C. before autoclaving.

Similar treatment of alumina at 105° C. for 20 days gave a product of widely varying composition, the water held after drying over lime varying between 1.3 and 2.3 moles of water per mole of Al_2O_3.

Determination of Combined and Uncombined Alumina

Preliminary experiments showed that hydrated alumina that had been autoclaved at 150° C. until its composition corresponded to approximately $Al_2O_3 \cdot 1.1H_2O$ was almost insoluble in boiling dilute hydrochloric acid. On the other hand, tricalcium aluminate hexahydrate dissolves quite readily in 5% hydrochloric acid at 65° C. These facts make a separation of combined and free hydrated alumina in the autoclaved products possible.

TABLE IV

ANALYSES OF ALUMINA–ALUMINATE MIXTURES AFTER AUTOCLAVING AT 150° C.

Vol. of 5% HCl, ml.	Time of digestion at 65° C., min.	Combined Al_2O_3 as percentage of total Al_2O_3	Free Al_2O_3		Combined Al_2O_3	
			Present, gm.	Found, gm.	Present, gm.	Found, gm.
16	8	100	None	None	0.1067	0.1068
33	8	53.6	0.2044	0.2043	0.2266	0.2244
20	5	20.5	0.2952	0.2934	0.0763	0.0761
42	5	10.0	0.2916	0.2923	0.0325	0.0333
15	8	0.0	0.2989	0.2978	None	—

Table IV gives the results of a series of experiments illustrating the accuracy one may expect in attempting a quantitative separation of free and combined alumina in autoclaved mixtures of alumina and tricalcium aluminate on the basis of their difference in solubility in 5% hydrochloric acid. The combined alumina in the products in terms of the total alumina varied from 0 to 100%. The procedure used was as follows: Mixtures of hydrated alumina and tricalcium aluminate of known composition were treated in platinum crucibles in an autoclave at 150° C. for 48 hr., then transferred into small beakers, any lumps broken up, a definite quantity of 5% hydrochloric acid added, and the mixture kept at 65° C. with stirring for a given interval of time. Cold ammonium chloride solution was then added and the undissolved residue filtered off and washed. The residue was ignited at 1100° C. to constant weight and the alumina in the filtrate determined by precipitation. The calculations were made on the assumption that all the alumina found in the filtrate had been in the combined form.

The method appears to give a good approximation for the combined and uncombined alumina in the autoclaved mixtures. After some further study it appeared that the best results were obtained on treatment of the powdered autoclaved mixture with a large excess of 5% hydrochloric acid for three minutes at 65° C., adding a cold solution of ammonium chloride, and filtering rapidly.

Analysis of the Autoclaved Aluminates of Calcium

Freshly ignited 1.5 gm. samples of the aluminates contained in platinum crucibles were treated in saturated steam in the gas heated copper autoclave at 150° C. for from 16 to 32 days, dried to constant weight over quicklime, and (a) the loss on ignition, and (b) combined and uncombined alumina, determined as described above.   The results are given in Table V.

TABLE V

ANALYSIS OF ALUMINATES OF CALCIUM HYDRATED AT 150° C.

(Gas heated autoclave)

Expt. No.	Days in auto-clave	5CaO·3Al₂O₃		CaO·Al₂O₃		3CaO·5Al₂O₃	
		Ign. loss, %	Comb. Al₂O₃, % of total Al₂O₃	Ign. loss, %	Comb. Al₂O₃, % of total Al₂O₃	Ign. loss, %	Comb. Al₂O₃, % of total Al₂O₃
H–3	32	33.2	57.4	31.7	33.8	28.4	19.6
H–4	21	33.8	56.9	31.4	34.5	28.6	20.1
H–5	19	34.0	57.1	30.9	34.5	28.0	20.6
H–6	16	33.8	56.5	30.5	33.7	28.3	20.0
Average		33.7	57.0	31.1	34.1	28.3	20.1
Calculated*		35.2	55.6	31.2	33.3	27.6	20.0

* Calculated values are on the basis of the formation of $3CaO·Al_2O_3·6H_2O$ and $Al_2O_3·1.1H_2O$. The ignition loss is calculated as percentage of anhydrous sample.

Microscopic examinations of the hydrothermally treated samples disclosed no unhydrated centres.   If present, these should be easily observed in the case of the mono- and 3 : 5-calcium aluminate but might be overlooked in the case of the 5 : 3 product, as this compound has a refractive index of 1.608 as compared with 1.604 for the hexahydrate of tricalcium aluminate.   Both this last substance and hydrated alumina could be readily identified in all the samples (observed values for refractive index, 1.605 ± 0.002 and 1.615 ± 0.005, respectively).   The autoclaved samples of the 5 : 3 aluminate contained in addition an appreciable quantity of a birefringent product having a refractive index of 1.580 ± 0.005, while the 1 : 1 and the 3 : 5 aluminates contained only traces of this material.   Positive tests for free calcium hydroxide were obtained by the anhydrous alcohol–glycerol extraction method, but it was found that hydrated alumina, which was present in large amounts, produces a similar change in the indicator.   The positive result is therefore questionable.

It was found that the autoclaved samples always contained very slight traces of calcite in spite of every attempt to prevent contamination with carbon dioxide.   The amounts of calcite increased with the time of treatment in the autoclave, although in all cases only small amounts were present.

Ultimately it was decided that the contamination was probably due to diffusion of carbon dioxide from the gas flame with which the autoclave was heated through the copper walls of the autoclave. After changing to electric heating the products were found to be entirely free from calcite. The results obtained in a series of treatments using electrical heating are given in Table VI.

TABLE VI

ANALYSES OF ALUMINATES AFTER 17 DAYS AUTOCLAVING AT 150° C.

Electrical heating

Aluminate	Ignition loss, %		Combined alumina, % of total alumina	
	Calculated	Found	Calculated	Found
$5CaO \cdot 3Al_2O_3$	35.24	33.91	55.55	57.40
$CaO \cdot Al_2O_3$	31.16	31.42	33.33	33.39
$3CaO \cdot 5Al_2O_3$	27.64	28.12	20.00	20.06

The autoclaved products from the last two aluminates of Table VI were almost free from birefringent crystals, while the product from the 5 : 3 aluminate contained an appreciable amount of material with a refractive index of about 1.58.

Considering the data of Tables V and VI, it is apparent that there is satisfactory agreement between the calculated and experimental values for the combined alumina in the case of the 3 : 5 aluminate, and that the corresponding agreement for the water taken up is quite good considering the uncertainty as to the hydration of the alumina. The same may be said about the monocalcium aluminate. The experimental results may therefore be interpreted on the assumption that the main products of the hydrothermal treatment of monocalcium aluminate and the 3 : 5 calcium aluminate under the conditions of these experiments are the hexahydrate of tricalcium aluminate and hydrated alumina (approximate composition: $Al_2O_3 \cdot 1.1H_2O$).

The calculated and analytical values for the 5 : 3 calcium aluminate differ materially, the experimental value for water of hydration being about 4% low and the value for combined alumina about 3% high. These results might be explained by incomplete hydration since this would lower the water held, while the undecomposed anhydrous aluminate would dissolve in the acid and thus raise the value for the soluble (combined) alumina. This explanation seems unlikely as the 16 and 32 day treatments give essentially the same values. Furthermore, a considerable amount of birefringent material of refractive index of about 1.58 is always present in the product.

The question of the accuracy of the method for determining combined alumina under the conditions present in the case of the 5 : 3 and 1 : 1 aluminates was investigated further. Precipitated alumina was mixed with the

pure hexahydrate of tricalcium aluminate so as to produce a mixture of the composition of the 5 : 3 and 1 : 1 calcium aluminates, respectively. The mixtures were then treated in the autoclave for several days at 150° C., dried over lime, and analysed, with the following results:

For the 5 : 3 mixture:—soluble alumina—found 55.41; calc. 55.51%.

For the 1 : 1 mixture:—soluble alumina—found 33.39; calc. 33.32%.

These results indicate that the discrepancy between the calculated and experimental values for $5CaO \cdot 3Al_2O_3$ in Tables V and VI is too large to be explained on the basis of analytical error.

Hydrothermal Treatment of the Aluminates at 105° C.

For the hydrations at 105° C. the samples were contained in small platinum crucibles supported above the water level in silver lined steel tubes, with air-tight covers. The tubes were heated in a constant temperature air oven. After treatment the samples were dried over lime and analysed with the results given in Table VII.

TABLE VII

Hydration of the Calcium Aluminates at 105° C.

Aluminate	Days in oven	Ign. loss, % on anhyd. basis	Combined Al_2O_3, % of total Al_2O_3	
			Found	Calc.*
$5CaO \cdot 3Al_2O_3$	29	39.24	59.80	55.55
$CaO \cdot Al_2O_3$	21	41.47	35.59	33.33
	23	43.36	35.65	
$3CaO \cdot 5Al_2O_3$	19	46.78	22.40	20.00
	23	44.26	22.08	

* *Calculated on the basis of the formation of soluble $3CaO \cdot Al_2O_3 \cdot 6H_2O$ and insoluble hydrated alumina, $Al_2O_3 \cdot 1.1H_2O$.*

The high and irregular values for the water taken up are to be expected from the results given above for the treatment of aluminium hydroxide at 105° C. The experimental values for combined alumina are all higher than the calculated values, indicating the presence of a low-limed hydroaluminate. Experiments indicated that the discrepancy cannot be due to the solubility of the free hydrated alumina after treatment at 105° C.

Microscopic examination of the products did not disclose any calcite but a considerable amount of anisotropic material of refractive index of about 1.58 was present. The hydrothermal products of the monocalcium aluminate contained a number of hexagonal plates with a refractive index of 1.576 ± 0.002 (sodium light at 25° C.) and well crystallized grains from which a value for $\epsilon = 1.589 \pm 0.002$ was obtained. The birefringence is therefore of the order of 0.013 and the optical character positive. It is probable that this represents the birefringent material found in all the hydrothermal products.

General Conclusions

The quantitative results obtained for the hydrothermal treatment of $5CaO \cdot 3Al_2O_3$ at 150° C. indicate that while the main products are the hexahydrate of tricalcium aluminate and a monohydrate of alumina, yet a low-limed hydroaluminate is also formed.   On the other hand both $CaO \cdot Al_2O_3$ and $3CaO \cdot 5Al_2O_3$ appear to hydrate at 150° C. almost quantitatively to the hexahydrate of tricalcium aluminate and the monohydrate of alumina.

The hydrothermal treatments at 105° C. (which may have favoured hydrolysis through alternate condensation of water on the solid aluminate and evaporation of same due to slight fluctuations in the oven temperature) gave both much higher absorption of water and higher soluble alumina than called for by the formation of the cubic hydrate of tricalcium aluminate and the monohydrate of alumina.   In addition, considerably larger amounts of the birefringent material of refractive index 1.58 was present in all the hydration products.   The high and irregular values for the absorption of water at 105° C. may be explained on the basis of the behaviour of the hydrated alumina at this temperature.   The high values obtained for combined alumina are probably due mainly to the formation of a hydroaluminate with a lower lime-alumina ratio than the hexahydrate of tricalcium aluminate.

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INHIBITION OF CORROSION OF ALUMINUM AND OTHER METALS IN SODA ASH SOLUTIONS[1]

By J. F. J. Thomas[2]

Abstract

Some previously reported curves showing the rate of attack on commercial 2S$\frac{1}{2}$H aluminum by $\frac{1}{2}$% (by weight) aqueous solutions of various salt–soda-ash mixtures were confirmed. The inhibitive action of various commercial silicates, sodium fluosilicate, and certain other salts in dilute soda ash solutions was determined with aluminum, duralumin, copper, tin plate, and galvanized iron. Of all the salts tested, sodium fluosilicate was found to be the most efficient inhibitor of attack on aluminum. At inhibition in 0.5% aqueous solutions of the sodium-silicate–soda-ash mixtures at 60° C. the ratio $SiO_2:Na_2CO_3$ and the ratio of silica to surface area of aluminum metal were both roughly constant with all the sodium silicates studied. With sodium fluosilicate, these same ratios are maintained when calculated on the basis of SiF_4. Increasing the temperature of solution above about 80° C. appears to increase these inhibition ratios, but the ratios hold at higher concentrations of the aqueous solution of the soda-ash–salt mixture than the 0.5% studied in detail.

In a previous paper (1) some test results of the corrosive action, on commercial sheet aluminum and aluminum utensils, of several proprietary dishwashing compounds and various mixtures of the salts commonly present in such compounds were reported. This work indicated that, of all the salts commonly mixed with soda ash in these compounds, sodium metasilicate was the most effective inhibitor of attack on aluminum. It was recommended that, in order to prevent any attack under various conditions, about 25% of the soda-ash–sodium-metasilicate mixture should be metasilicate when a $\frac{1}{2}$% solution of the salt mixture was used.

It has been reported elsewhere (2) that sodium fluosilicate (Na_2SiF_6) is even more effective than sodium metasilicate as an inhibitor of the attack by dilute soda ash solutions on aluminum.

This paper describes a study of sodium fluosilicate, various commercial silicates, and other salts as inhibitors of attack by soda ash solutions on aluminum, duralumin, copper, tin plate, and galvanized iron sheet.

Experimental

The test procedure was similar to that previously used except that the testing period was extended from one to two hours.

Previous work carried out to determine a suitable test procedure had shown that the following factors influenced (to varying degrees) the amount of attack:

(1) The surface condition of the metal,

(2) The ratio of metal surface area to the volume of corrosive medium,

(3) The duration of test period,

(4) The temperature of the test solutions,

and that somewhat erratic results were often obtained by the re-use of test panels, even when these had been re-etched, and that different sheets of the supposedly same aluminum alloy could show different amounts of attack.   In the present work, all test panels were used once only and (unless otherwise stated) all were cut from the same sheet of aluminum (sheet No. 5; thickness, 0.041 in.).

Panels of 2S½H commercial aluminum, approximately 4 by 5 cm., were washed in hot soapy water, dipped in petroleum ether, and then etched for two minutes in a cold aqueous 10% sodium hydroxide solution before testing. The amount of attack after exposure for two hours in the test solution was determined by the loss in weight of the panels.   The treatment of the panels of 17ST commercial duralumin sheet was similar to that of the aluminum. The tin plate and galvanized panels were simply washed by scrubbing in soapy water, dipped in petroleum ether, and dried.   The copper panels were similarly cleaned, and then etched for about one-half minute in 40% nitric acid.   All test panels were rewashed and dried after etching.

Unless otherwise indicated, each panel was totally immersed for two hours at $60 \pm 5°$ C. in an aqueous (distilled water) solution containing a total of 0.5% by weight of salt or salt mixture.   In these tests, the ratio of metal surface area to solution volume was the same as that previously used (1), namely, 2 sq. dm. per litre.

The soda ash solutions were prepared from c.p. anhydrous sodium carbonate, while the silicates used were all commercial products of the Philadelphia Quartz Co.   The term sodium metasilicate, as generally understood in practice, refers to the pentahydrate, $Na_2SiO_3.5H_2O$, which is sold under the trade name "Metso".   This is the same sodium metasilicate referred to in the previous paper (1).

Unless otherwise indicated, all other salts referred to were c.p. chemicals.

Results

Some results are shown graphically in Figs. 1 to 15, inclusive.

Fig. 1 shows the effect of changing the duration of the test period.   It will be noted that, using a slightly corrosive mixture of soda ash and sodium metasilicate (containing only 15% metasilicate), the curve of the loss in weight per unit area against the time of total immersion is quite typical, the rate of attack decreasing with time.   The slope of the curve is virtually linear up to three hours, so that increasing the testing time from one to two hours changes the total amount of corrosion only.

In Fig. 2 is shown the effect of a change in the ratio of the total surface area of the exposed aluminum to the volume of corrosive solution.   The
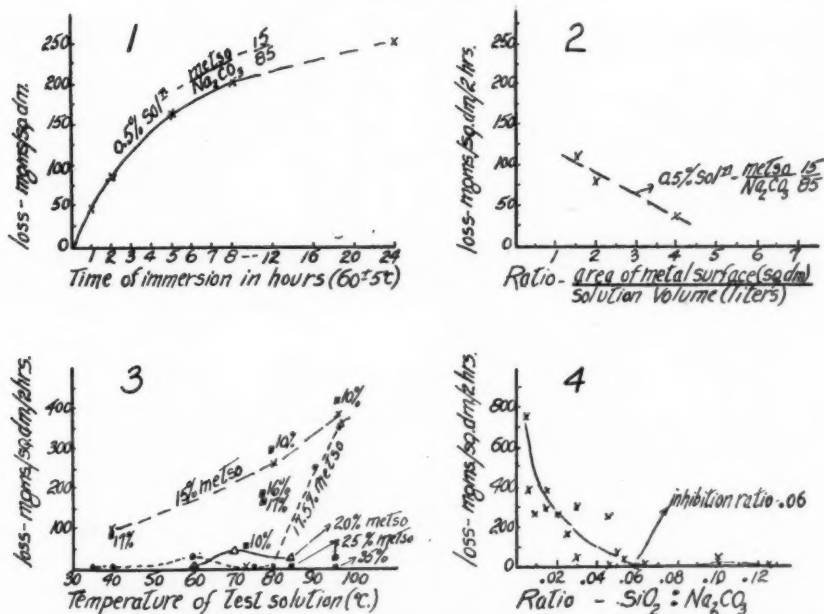
FIGS. 1, 2, 3, AND 4. *The effect of certain variables on the rate of attack on aluminum by mixtures of soda ash and sodium metasilicate in 0.5% aqueous solution of the mixture.*

attack increases with the decreasing ratio, that is, with a greater proportionate volume of solution.

The effect of changes in the temperature of the solutions is shown in Fig. 3. While some variability is noted, in general to avoid attack above 75 to 80° C. more silicate is necessary, with the ratio of silica to soda ash greater. It will be noted that a 0.5% solution of a salt mixture containing 15 to 16% metasilicate is corrosive at virtually all temperatures, and attack increases with increasing temperature.   When the percentage of silicate in the mixture is 17.5 or greater in the 0.5% solution, protection is generally found at temperatures up to about 80° C.; above this temperature, 20% or more of the silicate is necessary.

Fig. 4 shows the results obtained (at approximately 60° C.) with various ratios of silica to sodium carbonate in the mixtures in the 0.5% solutions. In this case the loss of weight per unit area is plotted against this ratio, and it is found that protection is obtained only when the ratio of silica to soda ash is about 0.05, 0.06, or greater.

In Figs. 5, 6, 7, 8, and 9 are shown results obtained using various commercial-silicates–soda-ash mixtures in 0.5% solutions of the mixtures.   Fig. 5 shows further results with sodium metasilicate (Metso).   This curve conforms quite well to that previously shown, and it is found that about 17% of Metso in the salt mixture is necessary to prevent attack on aluminum.
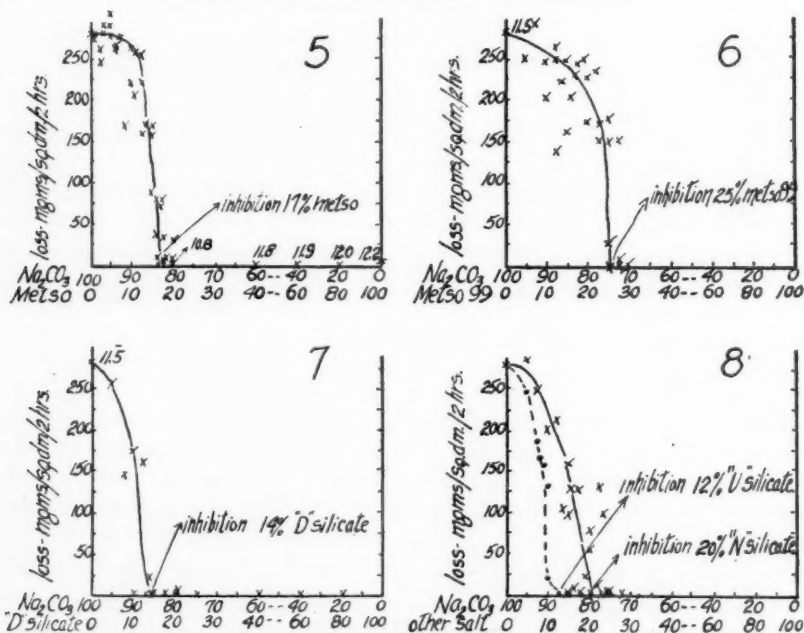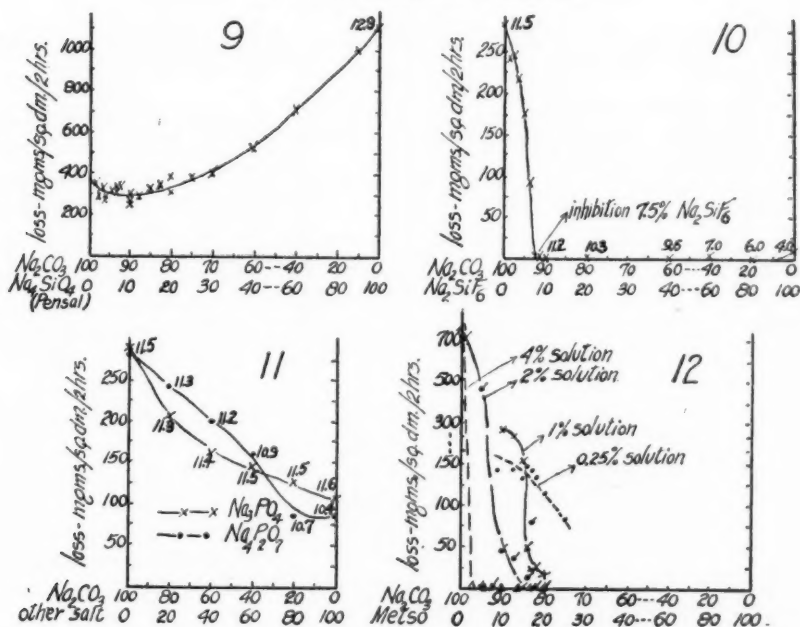
FIGS. 5, 6, 7, AND 8.   *The amount of attack on commercial aluminum by aqueous mixtures of soda ash and various silicates at 60 ± 5° C. for two hours.   Abscissae in above curves refer to the proportions of the salts present in an aqueous solution containing a total of 0.5% salt or salt mixture.   Figures accompanying points on the curves refer to the pH of 0.5% solutions of the proportions shown by the abscissae.*

Fig. 6 shows a similar curve obtained when various proportions of the commercial silicate "Metso 99" and soda ash in ½% solution were used. The inhibiting amount of silicate necessary is found to be about 25% of the salt mixture.   In Fig. 7 a similar curve obtained with "D" brand liquid silicate is shown.   The inhibiting amount of silicate necessary in this case is about 14%.   Twelve per cent of "U" and 20% of "N" brand liquid silicates, in mixtures with soda ash in 0.5% solutions, inhibit attack on aluminum, as shown by the curves in Fig. 8.

Fig. 9 shows some results obtained using mixtures of the commercial product "Pensal" (a sodium orthosilicate) and soda ash in ½% solution of the mixture.   It will be noted that in no case was any inhibition found with this silicate; in fact, increasing the amount of sodium orthosilicate above 25% of the mixture caused increasing attack on aluminum.

Fig. 10 shows that, with mixtures of sodium fluosilicate and soda ash in ½% solutions of the mixture, inhibition is obtained with as low as about 7.5% of sodium fluosilicate.

Fig. 11 shows, in confirmation of previous work (1), curves obtained using trisodium phosphate and sodium pyrophosphate respectively with the soda ash in 0.5% solutions of the mixture.

FIGS. 9, 10, AND 11. *The amount of attack on commercial aluminum by mixtures of soda ash and certain other salts in 0.5% aqueous solution at 60 ± 5° C. for two hours.* FIG. 12. *Similar curves with mixtures of soda ash and Metso in 0.25, 1, 2, and 4% aqueous solutions of the mixture. Abscissae refer to the proportion of salts present in the aqueous solution, and figures accompanying points on the curves refer to the pH of the solutions containing salts in the proportion shown in the abscissae.*

In Fig. 12 some results with mixtures of soda ash and Metso in solution concentrations of 0.25, 1, 2, and 4% of the mixture respectively are shown. Increasing the concentration of the solution appears to cause a decrease in the percentage of Metso necessary for inhibition. With the 0.25% solution a greater percentage of Metso than the 17% found with the $\frac{1}{2}$% solution of the mixture is required (Fig. 5).

Fig. 13 shows a few results on commercial tin plate. In this case Metso appears to offer no marked inhibition, while sodium fluosilicate in increasing proportions provides inhibition up to about 60% of the mixture with soda ash; the amount of attack rapidly increases again above this percentage. There is a zone of total inhibition between proportions of 40 to 60% sodium fluosilicate in the mixture.

In Fig. 14, results using Metso–soda-ash and sodium-fluosilicate–soda-ash mixtures on galvanized iron are shown. The amount of Metso necessary for inhibition is roughly 16 to 17% of the mixture, but in this case no inhibition is found with sodium fluosilicate; in fact, the attack is increased with increasing amounts of this salt. This is readily understood when it is recalled that zinc fluosilicate is soluble.
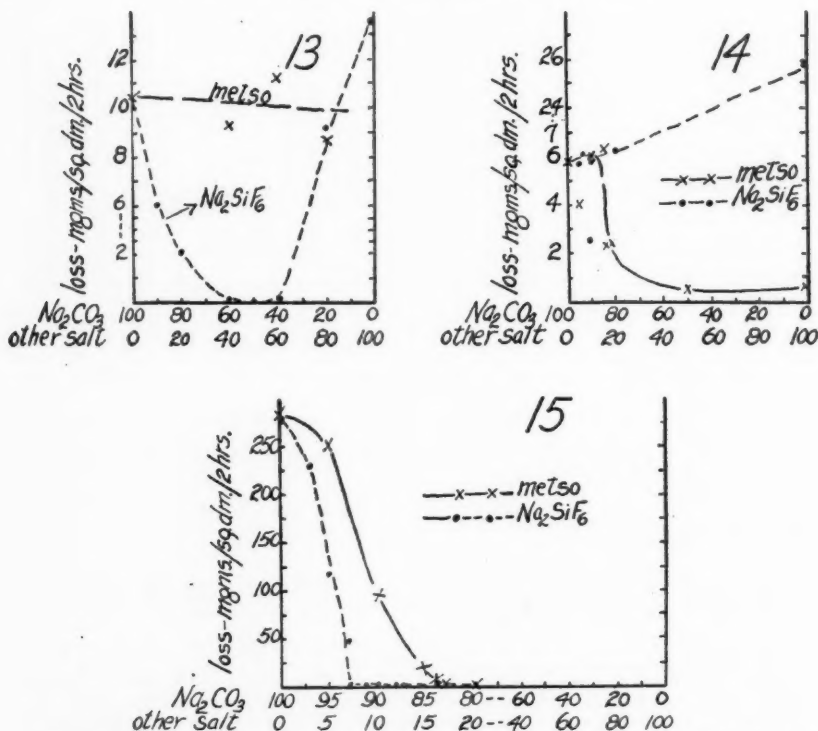
FIGS. 13, 14, AND 15. *Curves showing the amount of attack on tin plate (Fig. 13), gal-vanized iron (Fig. 14), and duralumin (Fig. 15) by mixtures of soda-ash–Metso and soda-ash–sodium-fluosilicate in 0.5% aqueous solution of the salt mixture.*

The attack on duralumin using $\frac{1}{2}\%$ solutions of (i) Metso–soda-ash mixtures and (ii) sodium-fluosilicate–soda-ash mixtures is shown in Fig. 15. With Metso, the amount necessary for inhibition of attack on duralumin is found to be about the same as that found with aluminum, that is, 16 to 17% of the mixture. Similarly with sodium fluosilicate, the inhibition proportion for duralumin is the same as for aluminum—7 to $7\frac{1}{2}\%$.

In no case with galvanized iron and tin plate is the attack severe. The small weight losses and the difficulty in cleaning the metals after exposure give rise to considerable error and variation in these results. This was found with copper also. The attack by the aqueous soda-ash–salt mixtures, while discolouring the copper in many solutions, in no case gave appreciable weight losses, and neither Metso nor fluosilicate exhibited any inhibition. In admixture with soda ash, the following substances were tried as inhibitors of attack on tin plate:—trisodium phosphate, sodium pyrophosphate, sodium phosphite, gelatin, sorbitol, sodium nitrite, hexamethylenetetramine, sodium orthosilicate and microcosmic salt. With none of these was the amount of

attack greater than about 14 mg. per sq. dm. after two hours at 60° C., and generally it was about 8 or 9 mg. per sq. dm. in two hours.

Influence of pH

In a number of the above curves and in Tables I and II, the approximate pH values of various solutions are shown. There is no apparent relation between inhibition and the pH of the solutions.

Discoloration of Aluminum

Previous work with sheet No. 1 of 2S½H aluminum indicated very little correlation between the amount of attack and discoloration of test panels. The present work with aluminum sheet No. 5, using fresh panels each time, indicated that when the loss of weight was high the panels usually were markedly discoloured. In general, three main types of discoloration were noted. First, a slight brown discoloration might be found with very little apparent etching of the aluminum surface; second, a more complete but streaky gray or brown covering, with marked etching on the metal surface; and third, a very uniform black or brown discoloration. The last was in many cases quite decorative, no structural etching being noted. Various mixtures of salts gave different colorations. For example, sodium salicylate, sodium nitrite, hexamethylenetetramine, and zinc sulphate, in proportions of 80 or 90% of the soda-ash–salt mixture in aqueous 0.5% solutions generally produced the third type of discoloration within from one to two hours. A few additional tests were carried out in an attempt to obtain this black or brown coating without producing any marked attack on the aluminum. No solution mixture producing this coating was found that would give less than 16 mg. loss in weight per sq. dm. after two hours at 60° C. The best solutions were mixtures of soda ash with 80% of sodium nitrite, 80% of hexamethylene-tetramine, 80% of sodium salicylate, 60% of sorbitol, 15% of Metso, or 20% of a sodium-fluoride–Metso mixture (50 : 50). In all these solutions, there was appreciable attack.

Table I shows that, in general, the minimum amount of actual silica (calculated from the determination of silica in each commercial product) necessary for inhibition per square decimetre of aluminum surface is of the same order—about 120 mg. The ratio of silica to soda ash at the limiting inhibition percentage in the mixture agrees very well in most cases with that shown in the other tests (Fig. 4), namely, 0.05 to 0.06. With sodium fluosilicate replacing silica by silicon tetrafluoride, approximately the same ratios are obtained as with the silicates. This may indicate that all these compounds function in the same manner as inhibitors of the action of sodium carbonate and depend on the actual amount of available SiO_2 or SiF_4. Perhaps a natural film of silica or silicon tetrafluoride is deposited on the aluminum metal surface. This agrees with the opinion of several other workers on the subject. The found ratios of silica to soda ash for soda-ash–sodium-orthosilicate mixtures would indicate that inhibition should be obtained at a proportion of about 14 to 15% of the orthosilicate in the salt mixture. This is

TABLE I

SODA-ASH–SODIUM-SILICATE SOLUTIONS

5 gm. salt per litre of aqueous solution

Silicate	Approximate theoretical SiO₂ content, %	SiO₂ from analysis, %	Approximate inhibition, from curves, %	No. mg. SiO₂ per 1 sq. dm. metal surface (from analysis), at inhibition	Ratio of SiO₂ to Na₂CO₃, at inhibition	pH of 0.5% solution
"Metso" $Na_2SiO_3.5H_2O$	28.3	28.6	17.0	121.5	0.059	12.2
"Metso 99" $3Na_2O.2SiO_2.11H_2O$	23.8	22.8	25.0	142.5	0.076	12.3
"N" Brand liquid silicate 41° Bé. $\dfrac{Na_2O}{SiO_2} = \dfrac{1}{3.22}$	28.7	28.9	20.0	144.5	0.072	10.6
"D" Brand liquid silicate 50° Bé. $\dfrac{Na_2O}{SiO_2} = \dfrac{1}{2.00}$	—	29.7	14.0	104	0.048	10.9
"U" Brand liquid silicate 52° Bé. $\dfrac{Na_2O}{SiO_2} = \dfrac{1}{2.40}$	33.1	37.8	12.0	113.4	0.052	10.6
"Pensal" (Na_4SiO_4)	32.6	—	—	—	—	12.9
Sodium fluosilicate as Na_2SiF_6	55.4*	—	7.5	103.9*	0.045*	3.5
				Av. 121.6	Av. 0.059	

* *Calculated as SiF₄.*

not found to be so (Fig. 9), and apparently the orthosilicate does not behave in the same way as the other silicates.

There is some difference between the above ratios when different silicates are used, but considering (i) the large number of variables and their effect as pointed out in Figs. 1, 2, 3, and 4, (ii) the usual erratic nature of corrosion tests with aluminum, and (iii) inherent experimental errors, the above agreement is thought to be sufficient to justify the above conclusions.

Confirmation of these conclusions is afforded in Fig. 12, which shows results obtained with varying proportions of Metso and soda ash mixtures, in increasing concentrations of the mixture in solution. The percentage of Metso that is necessary in the salt mixture for inhibition of attack decreases as the concentration of the salt mixture in solution increases. Thus, when mixtures of 4% soda ash and 4% Metso are used, only a very small quantity—

about $2\frac{1}{2}\%$ of silicate—is required to provide the necessary amount of silica (approximately 120 mg. per sq. dm. of metal surface).

Tests similar to those carried out with the Metso and sodium fluosilicate were also made with aluminum sheet No. 5, using a large number of other salts in various mixtures with soda ash (Table II). It was found that in comparison with sodium fluosilicate or sodium metasilicate, none of these salts, except sodium chromate (which was not considered because of its toxic nature and its effect on the skin), were efficient inhibitors of attack on aluminum. However, several of these compounds, especially sodium bisulphite, sodium metabisulphite, hexamethylenetetramine, sodium phosphotungstate, sodium pyrophosphate, etc., do show inhibition when present in higher proportions of the mixtures in $\frac{1}{2}\%$ solution. Most of the other salts showed no inhibition other than that due to dilution of the soda ash, they themselves being less corrosive than the sodium carbonate.

TABLE II

INHIBITING EFFICIENCY OF VARIOUS SALTS IN AQUEOUS SODA ASH SOLUTIONS AT 60° C.

Compounds tested with soda ash in 0.5% aqueous solution of the salt mixture	pH of 0.5% aqueous solution of compound	Remarks re rate of attack on aluminum by 0.5% solution of the Na$_2$CO$_3$–salt mixture
1. Gelatin	—	Erratic attack: inhibition at times with 40%, or more, of gelatin
2. Hexamethylenetetramine	8.1	Some inhibition: attack decreases more rapidly than with sodium pyrophosphate (Fig. 11)
3. Sorbitol	6.6	No marked inhibition at or below 60%
4. Urea	7.9	No marked inhibition at or below 20%
5. Microcosmic salt	8.0	Decreasing attack: inhibition at 80%
6. Trisodium phosphate	11.7	Fig. 11
7. Sodium pyrophosphate	10.4	Fig. 11
8. Sodium phosphite	8.0	Decreasing attack: more inhibition than with sodium pyrophosphate
9. Sodium hexametaphosphate (Calgon)	—	Decreasing attack: near inhibition at 50 to 100%
10. Sodium phosphotungstate	6.5	Inhibition at 60% or more
11. Sodium chromate	7.7	Good inhibition at 10% or more
12. Sodium nitrite	6.7	Decreasing attack–not quite as rapid inhibition as with Na$_4$P$_2$O$_7$
13. Sodium sulphate	—	Decreasing attack–no marked inhibition at and below 30%
14. Sodium salicylate	—	Decreasing attack–more rapid inhibition than with Na$_4$P$_2$O$_7$
15. Sodium fluoride	—	Increasing attack up to 20%
16. Sodium fluoride + Metso (50 : 50)	—	No marked inhibition up to 25%, but more rapid decrease in attack than with Na$_4$P$_2$O$_7$
17. Sodium nitrite + Metso (50 : 50)	—	No marked inhibition at and below 10%
18. Sodium acid sulphite	2.8	Decreasing attack–inhibition at 60% or slightly less
19. Sodium metabisulphite	3.0	Decreasing attack–inhibition at about 45%
20. Zinc sulphate	5.9	Precipitate forms with Na$_2$CO$_3$. Decreasing attack. Inhibition at 60% or more

Mixtures of soda ash and sodium-fluoride–sodium-metasilicate (50 : 50) were tried in an attempt to learn whether the fluoride exerted any cleaning or minor etching of the aluminum that would allow more efficient action by the silicate. This was at first thought to be a possible reason for the inhibitive efficiency of sodium fluosilicate. There was found to be no advantage in using the sodium-fluoride–Metso (50 : 50) mixture instead of an equivalent amount of Metso alone.

The mixture of sodium nitrite and Metso (50 : 50) was tried since this has been recommended by certain Russian workers as an inhibitor in aqueous soda ash solutions. There was no advantage in its use instead of an equivalent amount of Metso alone.

Summary

1. Previous curves showing the efficiency of certain salts as inhibitors of attack by soda ash solutions on aluminum have been confirmed.

2. It is shown that inhibition by sodium fluosilicate is more efficient than that by sodium metasilicate—a lower percentage of the former gives protection.

3. Most commercial silicates, except sodium orthosilicate, are inhibitors of attack on aluminum by soda ash solutions. The amount of silicate necessary for protection depends on the actual silica content of the silicate, and at inhibition in 0.5% solutions of the salt mixture the amount of silica in milligrams per square decimetre of metal surface is virtually constant (120 to 140 mg. of silica per sq. dm. of metal surface). The ratio of silica to soda ash in the solution must also be maintained above about 0.05 in order to obtain protection.

4. At inhibition with sodium fluosilicate the amount in milligrams of silicon tetrafluoride per square decimetre of metal surface in 0.5% solutions of salt mixtures corresponds to the amount of silica when silicates are used.

5. The results of these experiments indicate that inhibition by these salts is due to a film of silica or silicon tetrafluoride on the metal surface.

6. No marked correlation between the pH of the solutions and inhibition was noted.

7. It was found that, in general, when attack was appreciable the aluminum panels were discoloured; some of these coatings are quite decorative.

8. Increasing the temperature above about 75 to 80° C. apparently necessitates an increase in the ratio of silica to metal surface and the ratio of silica to soda ash required for protection.

9. Increasing the concentration of the solution of the salt mixture decreases the amount of the inhibiting salt necessary for protection. It is necessary only that the above ratio of silica to metal surface be maintained. Increasing the amount of test solution in relation to metal surface causes increased attack.

10. It is indicated that attack on tin plate is inhibited by sodium fluosilicate only when this salt is present in amounts of 40 to 60% of the 0.5% solution of the mixture.

11. Duralumin apparently reacts similarly to aluminum, protection being afforded by Metso and sodium fluosilicate when the salt concentrations are the same as those required for the protection of aluminum.

12. Attack on galvanized iron by soda ash solutions is inhibited similarly to the attack on aluminum by Metso, but not by sodium fluosilicate, probably because the galvanized coating forms a soluble zinc fluosilicate.

13. Inhibition of attack on aluminum with Metso–soda-ash mixtures in $\frac{1}{2}\%$ solutions at temperatures of 60° C. is obtained when the amount of Metso is not less than 16 to 17% of the mixture, and to obtain protective inhibition near the boiling point the amount of Metso in the mixture should be at least 20 to 25%. These are about the same concentrations previously recommended. Similarly, sodium fluosilicate should be used commercially in slightly higher proportions of the soda-ash–sodium-fluosilicate mixture than that found necessary at about 60° C. ($7\frac{1}{2}\%$). Care should be exercised in using sodium fluosilicate for cleaning cooking utensils, etc., until more information is available regarding its toxicity.

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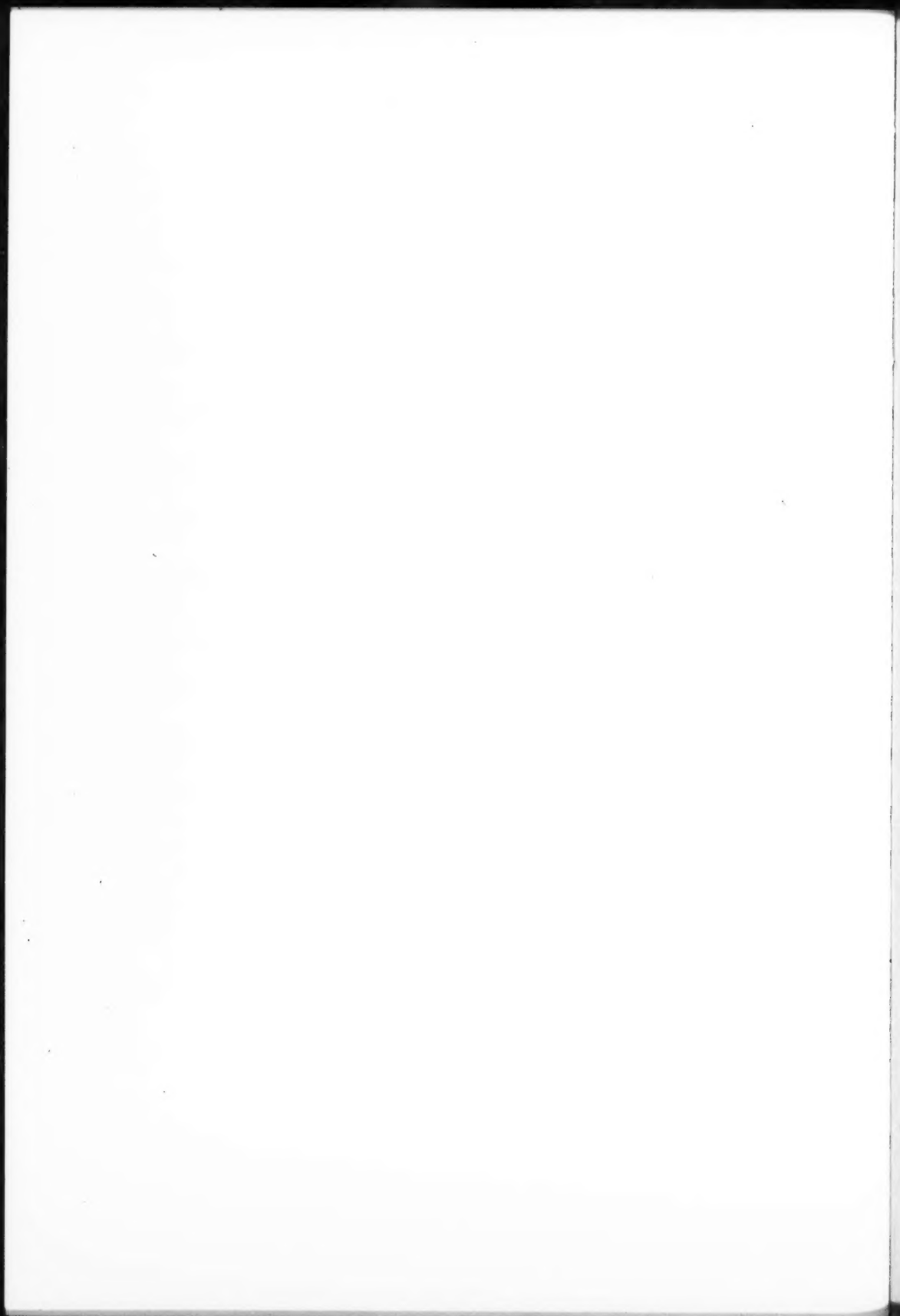
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